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Methanol Synthesis

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Abstract

This paper reviews the results of many years work in ICI into the kinetics and mechanism of methanol synthesis over copper/zinc oxide/alumina and other oxide supported catalysts. It was carried out under the precept that an understanding of the mode of action of the catalyst was a pre-requisite to the systematic improvement of the catalyst. The kinetics and mechanism of methanol synthesis over the multicomponent catalyst have been elucidated by the following process. The adsorptive and reactive interactions of each of the gas phase species (CO, CO_2, H_2) with each of the catalytic components (Cu, ZnO, Al_2O_3) separately have been studied. The interactions of combinations of the gas phase species with the individual catalytic components and then with pairs of the catalytic components etc were then studied, ultimately building up to a study of the full system. What has emerged is that it is the CO_2 component of the CO, CO_2 mixture which is the immediate precursor to methanol, being adsorbed on the partially oxidised copper as a symmetric carbonate. This carbonate is hydrogenated on the copper component of the catalyst to a formate species, the most stable and longest lived intermediate to methanol, hydrogenation of the formate being the rate determining step of the reaction. The specific activity of copper in synthesising methanol is unaffected by the nature of the oxide support, indicating that no unique synergy attaches to the copper/zinc oxide combination. The role of the CO is to keep the copper in a more reduced (more active) state than could be achieved with hydrogen alone.

INTRODUCTION

The synthesis of methanol over copper/zinc oxide/alumina catalysts is now so well established industrially as to be virtually self evident. It is, therefore, barely credible to reflect that as recently as 1923 methanol was produced by the distillation of wood. (The ecological benefits of catalysis are amply demonstrated by this system.) It was in 1923 that the German company Badische Anilin und Soda

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Fabrik (BASF) discovered that methanol was the major product of the hydrogenation of carbon monoxide over mixed zinc and chromium oxides (1). Although copper based catalysts were discovered shortly after (2), they were regarded for the next 38 years as being of "only slight practical interest" due to their short life (3). This resulted from two sources: (i) from their being readily poisoned and (ii) even in the absence of poisons from some intrinsic instability.

It was in 1966 that ICI discovered a method of preparation of these catalysts which overcame their intrinsic instability (4). This, and the change to a purer feedstock by switching from coal to natural gas as the source of synthesis gas, established the now familiar process.

A considerable effort has been, and is continuing to be, expended within ICI relating parameters of the preparation e.g. ageing time, ageing temperature, precursor crystallography etc. to the final activity and selectivity. For obvious commercial reasons, all of this work has gone unpublished. Nevertheless, a considerable body of work presently exists in the literature which relates the method of preparation of the catalyst to the nature of the active centre and ultimately to the activity of the catalyst itself. A considerable part of this body of work was instigated by Klier and his co-workers (5-9).

Briefly, using quantified X-ray diffraction, they claimed to show that a small amount of the copper (e.g. 2% in a 15% CuO/85% ZnO catalyst) was dissolved in the zinc oxide component of the catalyst (5). After reduction, the amount of copper dissolved in the zinc oxide was thought to increase to 12% in the copper/zinc oxide catalysts and to 16% in copper/zinc oxide/alumina catalysts (7). The copper was considered to be incorporated into the zinc oxide lattice as Cu^{+}, its being isoelectronic with Zn^{2+} (5). The Cu^{+} dissolved in the zinc oxide lattice was thought to be the active centre at which carbon monoxide was strongly adsorbed and sequentially hydrogenated to methanol. The role of carbon dioxide in the carbon monoxide/carbon dioxide/hydrogen feed was considered to be that of an oxidant, maintaining the active centre in the Cu^{+} state (5).

This view of the mechanism of the reaction gained a fairly general acceptance on two counts: (i) it accorded with a certain intuitive logic about the nature of the synergy which appeared to exist between copper and zinc oxide in respect of methanol synthesis, and (ii) it also explained why carbon monoxide should be the direct precursor to methanol. (The direct hydrogenation of carbon dioxide to methanol proposed by Kagan et al (10) appeared to be too costly energetically in that it required the breaking of the C-O bond in carbon dioxide, a process requiring ~116 kcal mol^{-1}. In spite of the experimental evidence to the contrary using labelled carbon monoxide, which produced methanol with the same specific activity as that of the carbon dioxide and showed incontrovertably that carbon dioxide was the direct precursor, the work of Kagan et at (10) went largely ignored.)

This paper reviews the results of many years work in ICI. It has involved a detailed study of the kinetics and mechanism of methanol synthesis over copper/zinc oxide/alumina and other oxide-supported copper catalysts. It was carried out under the precept that an understanding of the mode of action of the catalyst was a pre-requisite to the systematic improvement of the catalyst.

Methanol is generally made from $CO/CO_2/H_2$ (10:10:80) mixtures over a $Cu/ZnO/Al_2O_3$ (60:30:10) catalyst at ~250°C and between 50-100 bar. The kinetics and mechanism of its synthesis have been elucidated by the following process. The

adsorptive and reactive interactions of each of the gas phase species with each of the catalytic components, separately have been studied. This was followed by a study of the interactions of gas phase mixtures with the individual catalytic components etc, ultimately building up to a study of the full system.

2. THE ZINC OXIDE COMPONENT

Since zinc oxide was the original methanol synthesis catalyst discovered by (BASF) in 1923 (1) it was necessary first to study this component of the catalyst as a base experiment.

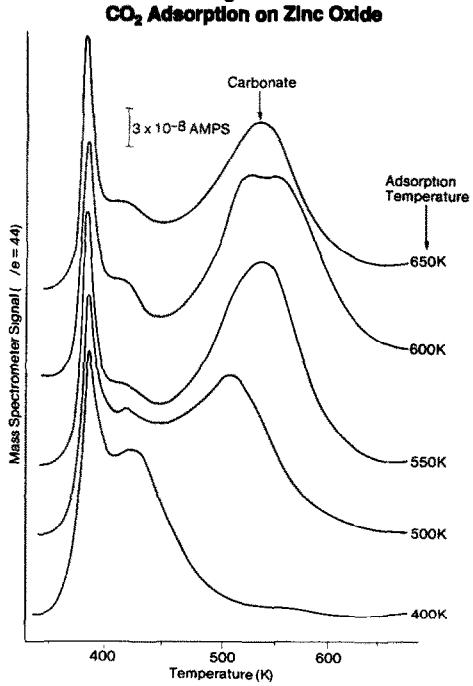
2.1. CO/ZnO Adsorption

Carbon monoxide is weakly held $\Delta H \sim 4.0$ kcal mol^{-1} with concomitant low surface coverage of $\sim 10^{-5}$ of a surface monolayer at 250°C (11).

2.2 CO_2/ZnO Adsorption

Carbon dioxide is strongly held on zinc oxide with four distinctly different kinds of bond whose energies are 26, 28, 34 and 37 kcal mol^{-1} (12). The former two bonds are thought to be carboxyl-type species while the latter two are thought to be carbonates. The evidence for this energetically heterogeneous bonding of CO_2 to the ZnO surface is shown in the temperature programmed desorption spectra of CO_2 from ZnO in Figure 1, the bond energies listed above being derived from the different peak maximum temperatures.

Figure 1
CO_2 Adsorption on Zinc Oxide



2.3. H_2/ZnO Adsorption

Hydrogen like CO_2 is adsorbed on to the ZnO surface by a multiplicity of bonds of different energy (12). Figure 2 shows the H_2 desorption spectra from ZnO, the three peak maxima being evidence of three distinctly different types of band. The low temperature states (peak maxima temperatures (T_m) 150°C (420K) and 192°C (465K), $E_{desorption}$ = 28 and 31kcal mol^{-1}) are thought to derive from dissociative adsorption of hydrogen across the ZnO pair

i.e. $ZnO + H_2 \rightleftarrows ZnH + OH$

while the high temperature state (T_m = 270°C (540K), $E_{desorption}$ = 36 kcal mol^{-1}) is thought to result from adsorption of hydrogen on the polar face and its subsequent migration along the c-axis of the crystal (Figure 3) into the bulk of the solid.

Figure 2
Temperature Programmed Desorption Spectra of Hydrogen from Zinc Oxide at Different Adsorption Temperatures

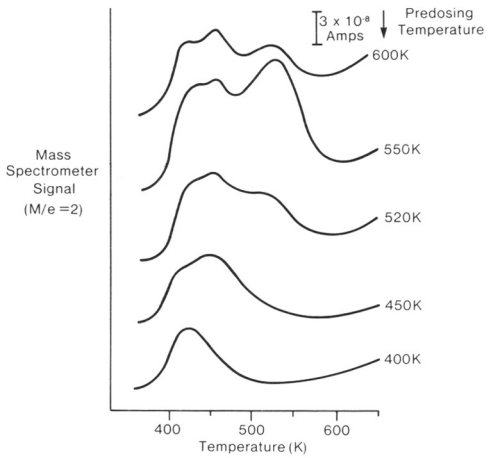
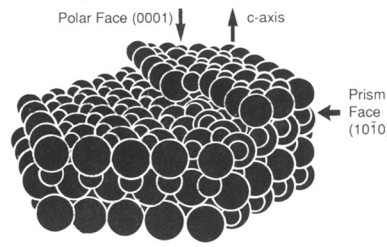


Figure 3
Crystal Faces of Zinc Oxide



2.4. H_2/CO/ZnO Co-adsorption and Reaction

The co-adsorption of H_2 and CO, at temperatures below which reaction occurs, results in a weakening of the already weak CO-ZnO interaction, the bond strength being halved to 1.9 kcal mol^{-1} while the coverages are reduced by a factor 10 to 10^{-6} of a monolayer (11).

When the temperature is raised to values at which reaction occurs (>250°C), the only product of the CO/H_2 interaction with zinc oxide is CO_2. No methanol was observed. The amount of the CO_2 produced was finite since the zinc oxide could be reduced to a given extent (~6% oxygen vacancies greater than produced by hydrogen pre-reduction) only under these conditions.

2.5. $H_2/CO_2/ZnO$ Co-adsorption

At temperatures above 130°C the co-adsorption of CO_2 and H_2 results in: (i) the annihilation of all the low temperature <250°C (<500K) states for the desorption of H_2 and CO_2 shown in Figures 1 and 2 and (ii) the formation of a new species, the formate species ($HCO_{2(a)}$), evidenced by the coincident desorption of H_2 and CO at 310°C (580K) (Figure 4) (12). The zinc oxide surface had been previously characterised for the desorption of a formate species by the adsorption and subsequent temperature programmed desorption of methyl formate. On adsorption the methyl formate dissociated into methoxy and a formate species, the latter being characterised by the coincident desorption of CO and H_2 at 310°C (580K) (Figure 5) (13).

Figure 4
Product Distribution after H_2/CO_2 Co-adsorption on Zinc Oxide at 500K

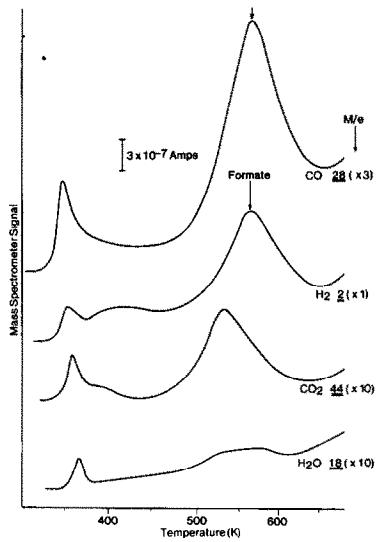
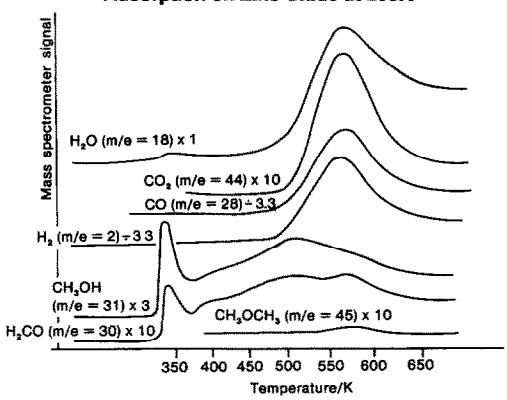


Figure 5
Product Distribution after Methyl Formate Adsorption on Zinc Oxide at 295K


Mass spectrometer signal
H2O (m/e = 18) x 1
CO2 (m/e = 44) x 10
CO (m/e = 28) ÷ 3.3
H2 (m/e = 2) ÷ 3.3
CH3OH
(m/e = 31) x 3
H2CO (m/e = 30) x 10
CH3OCH3 (m/e = 45) x 10
350 400 450 500 550 600 650
Temperature/K

2.6. HCHO/ZnO Adsorption and Reaction

The adsorption of formaldehyde (HCHO) at room temperature on zinc oxide and its subsequent desorption by temperature programming (Figure 6) shows evidence for the existence on the zinc oxide surface of the following species:

(i) molecular HCHO,
(ii) a methoxy species ($CH_3O_{(a)}$), evidenced by the coincident desorption of H_2, HCHO and CH_3OH at 110°C (380K), and

(iii) a formate species ($HCO_{2(a)}$), evidenced by the coincident desorption of H_2 and CO at 580K (3).

The interesting point about this spectrum is that when the formate begins to decompose and the hydrogen from it becomes mobile on the surface, some of the hydrogen can collide with the adsorbed formate ultimately forming methanol. The formate species is the most stable and therefore the pivotal intermediate in the formation of methanol on zinc oxide. It is formed from the interaction of CO_2 and H_2 on the zinc oxide and not from CO and H_2 (12).

Figure 6
Product Distribution after Formaldehyde Adsorption on Zinc Oxide at 295K

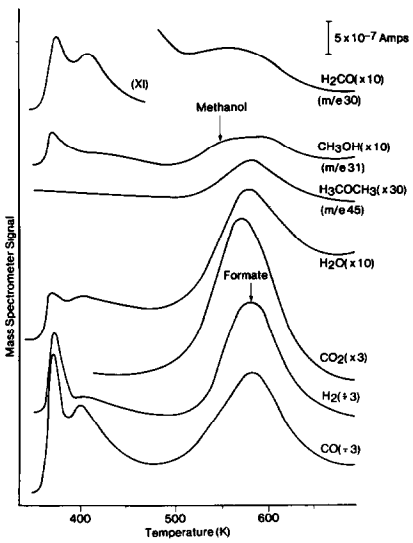
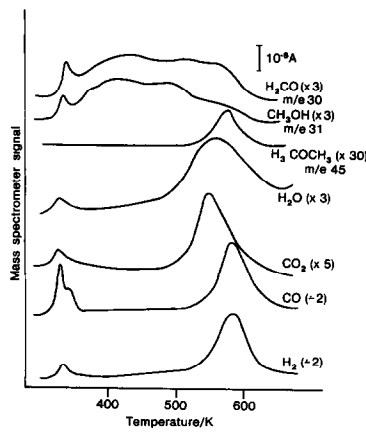


Figure 7
Product Distribution after Methanol Adsorption on Zinc Oxide at 295K



2.7. CH_3OH/ZnO Adsorption and Reaction

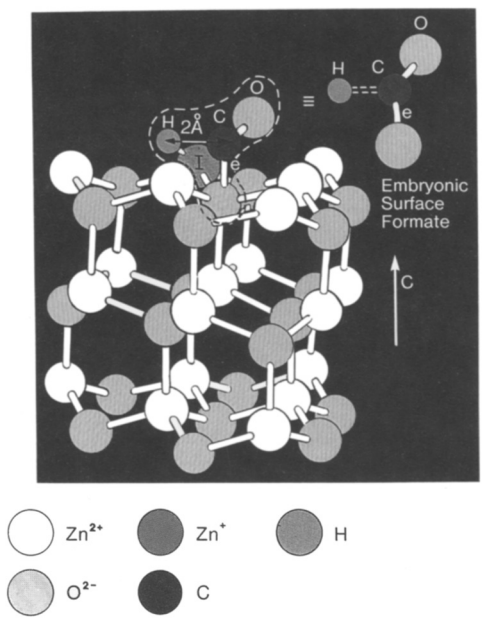
The adsorption of methanol on zinc oxide like that of formaldehyde results in the formation of adsorbed methoxy and formate species (12) evidenced in the temperature desorption spectrum (Figure 7) by the coincident desorption of H_2, HCHO and CH_3OH at 110°C (~380K) (methoxy) and by the coincident desorption of H_2 and CO at 310°C (580K) (formate). Since formate is involved both in the decomposition and synthesis of methanol it is a true intermediate in the reaction.

2.8. $CO_2/H_2/ZnO$ Reaction

The interaction of CO_2 and H_2 with zinc oxide at temperatures greater than 250°C

produces methanol (11). However, if the zinc oxide surface has an increased number of oxygen anion vacancies deriving from having been pre-reduced in a CO/H_2 mixture (section 2.4) the rate of methanol synthesis is increased initially, but transiently, by a factor of 50 over that produced at steady state from the CO_2/H_2 mixture. It is apparent from this evidence and from that presented in sections 2.5, 2.6 and 2.7 that the mechanism of methanol synthesis over the zinc oxide catalyst is by CO_2 adsorption at an anion vacancy on the surface where it is hydrogenated to a formate species (Figure 8) which is the most strongly held species in methanol on zinc oxide. This formate species is then hydrogenated through methoxy to methanol which desorbs leaving an oxygen behind to heal the vacancy. The role of the CO is to remove the oxygen from that site to produce the vacancy, hydrogen being a less powerful reducing agent than CO maintains a lower standing surface concentration of vacancies and therefore a lower activity.

Figure 8
The Interaction of CO_2, Adsorbed as CO_2^- at an Anion Vacancy, with Hydrogen Atoms on the Zinc Dominated Polar Face of Zinc Oxide



3. THE COPPER COMPONENT

For many years, indeed until the last few years, it was believed that copper alone was inactive in methanol synthesis (3, 6-9). In the light of the work detailed below, this view has now been revised and copper is acknowledged as the active component of copper/zinc oxide/alumina catalysts and is intrinsically active in its own right.

3.1. CO/Cu Adsorption

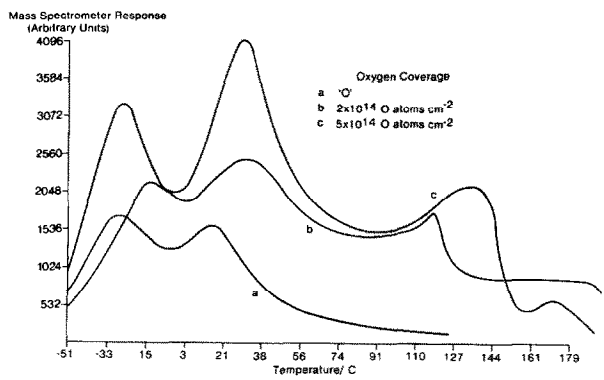
The adsorption of carbon monoxide on copper has been well studied by surface science. Single crystal studies have shown the heat of adsorption to be somewhat structure sensitive, having values of 13 kcal mol^{-1} on the (110) face (14), 10-12 kcal mol^{-1} on the (111) face (15, 16) and 12.5 kcal mol^{-1} on the (100) face (17).

3.2. CO_2/Cu Adsorption

Surprisingly CO_2 has been found to dissociate on adsorption on polycrystalline copper (18). The maximum amount of oxygen left on the surface after the CO_2 decomposition was only 25% of a monolayer, suggesting that the reaction might be structure sensitive. This has been confirmed by Fu and Somorjai (19) who found that CO_2 did not decompose on the low index (110) face but did decompose on the stepped (311) surface.

On a polycrystalline copper surface, pre-oxidised to half monolayer coverage with oxygen atoms by N_2O decomposition, the majority of the CO_2 is weakly held ($\Delta H \sim 4.5$ kcal mol^{-1}). However the adsorbed oxygen does produce a few (<3% of a monolayer/of high energy sites for CO_2 adsorption, evidenced by the appearance of higher temperature desorption states in the temperature programmed desorption spectrum as the oxygen atom coverage is increased (Figure 9) (20).

Figure 9
CO_2 Desorption Spectra from Oxygen Free and Partially Oxidised Copper



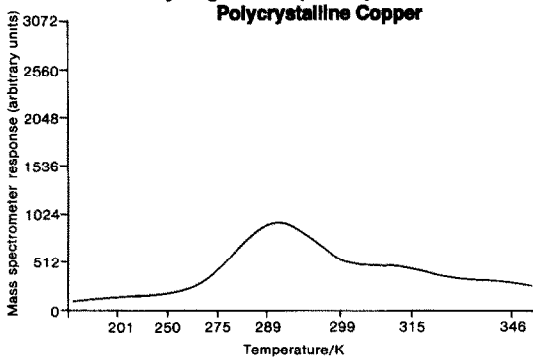
3.3. H_2/Cu Adsorption

The adsorption of hydrogen on copper has proved to be problematical. Until quite recently some authors believed that hydrogen did not chemisorb on copper (21). However, using molecular beam studies Balooch and Stickney showed that the difficulty in adsorbing hydrogen on to copper derived from the process having to overcome an activation barrier. This barrier they found to be structure sensitive, having a value of 3 kcal mol^{-1} on the (100) face and 5 kcal mol^{-1} on the (310) face (22). Recently, Hayden et al (23) using cold seeded molecular beams i.e. molecular beams of hydrogen in which the vibrational state is excited but in which the translational energy is reduced by the addition of a heavier atom (He), showed that

the energy barrier to hydrogen adsorption was not translational but vibrational.

The desorption energies of hydrogen from copper single crystal surfaces show the bond strength to be structure sensitive, having values of 13.2 kcal mol^{-1} on Cu(110) (24) (peak maximum temperature 93°C (336K)) and of 8.8 and 11.8 kcal mol^{-1} on Cu(111), corresponding to desorption peak maxima of -40°C (230K) and 27°C (300K) (25). The peak maximum temperature of hydrogen from polycrystalline copper is approximately 20°C (290K), the peak being broad, suggesting that the material comprises the (110) and (111) faces (Figure 10).

Figure 10
Hydrogen Desorption Spectrum from Polycrystalline Copper



Finally, Rieder and Stocker (26) have found that room temperature adsorption of hydrogen on Cu(110) initially causes a subsurface reconstruction of the copper atoms, observable by low energy electron diffraction but not seen by helium atom scattering. The conclusion is therefore that the hydrogen atoms adsorb and move below the surface causing the reconstruction. Low temperature adsorption of hydrogen <-30°C (<240K) allows observation of surface hydrogen by helium atom diffraction, but these migrate below the surface at temperatures greater than this, showing this migration to be activated.

3.4. $CO/H_2/Cu$ Co-adsorption

The co-adsorption of hydrogen with carbon monoxide on copper has no effect on the strength of bonding of the CO to the Cu (11). Figure 11 shows the adsorption isotherms for CO co-adsorbed with hydrogen on polycrystalline copper in the temperature range 100 to 130°C obtained by gas adsorption chromatography. The derived isosteric heats (Figure 12) are 12.5 ± 0.3 kcal mol^{-1} in the coverage range 0.38 x 10^{14} to 1 x 10^{14} molecule cm^{-2}, showing the polycrystalline copper to be low index face dominated (27).

Figure 11
CO Adsorption Isotherms on Reduced AnaLaR Cupric Oxide when CO-adsorbed with H_2

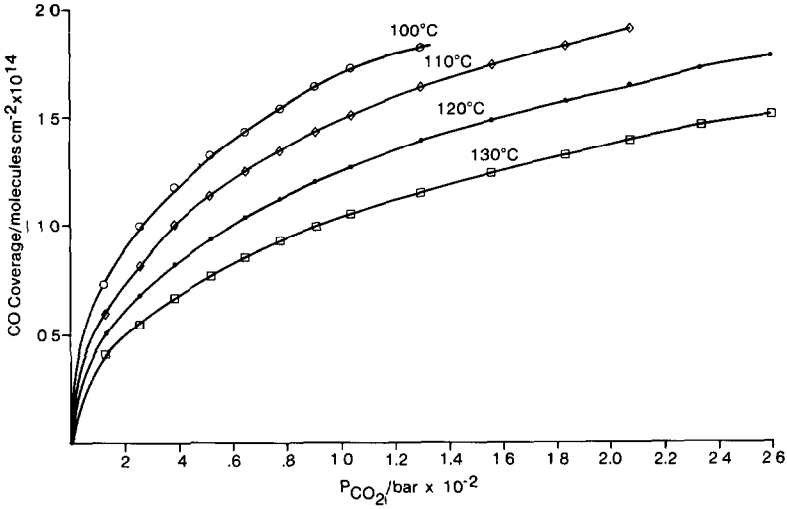
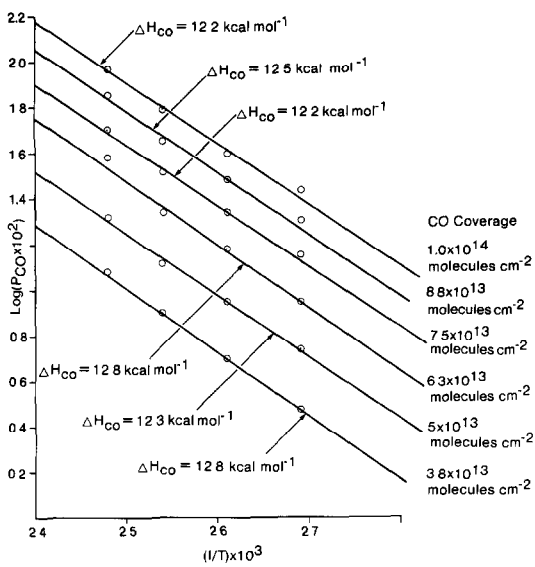


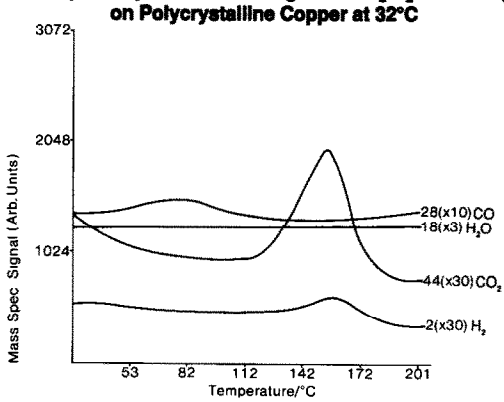
Figure 12
Isosteric Heats of Adsorption of CO on Copper when Co-adsorbed with H_2



3.5. $CO_2/H_2/Cu$ Co-adsorption

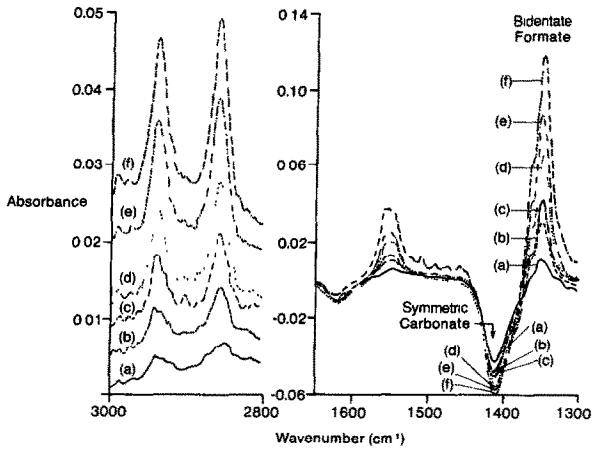
The co-adsorption of hydrogen and carbon dioxide on copper results in the formation of a formate species characterised by the coincident desorption of CO_2 and H_2 at 170°C (~440 K) (Figure 13) (28). Ying and Madix (29) first identified this coincident desorption of hydrogen and carbon dioxide at 170°C (440K) as formate following the adsorption of formic acid on a copper (110) surface.

Figure 13
Desorption Spectrum resulting from CO_2/H_2 Co-dosing on Polycrystalline Copper at 32°C



The mechanism of the formation of the formate from CO_2/H_2 co-adsorption has been elucidated by time dependent infra-red spectroscopy (30). Figure 14 shows the difference spectra obtained by co-dosing CO_2 and H_2 at room temperature on to silica supported copper, subsequently raising the temperature to 120°C in the gas. The symmetric carbonate species (the band at 1410 cm^{-1}) decreases with increasing time of exposure (curves a-f) while the bidentate formate species (the band at 1350 cm^{-1}) shows a proportionate increase. The mechanism for the formation of the formate therefore is:- (i) dissociative adsorption of CO_2, (ii) adsorption of the CO_2 onto the oxided surface to form the symmetric carbonate and (iii) hydrogenation of the symmetric carbonate to the bidentate formate. The band at 1350 cm^{-1} had previously been characterised as a bidentate formate by the adsorption of formic acid on the silica supported copper (31).

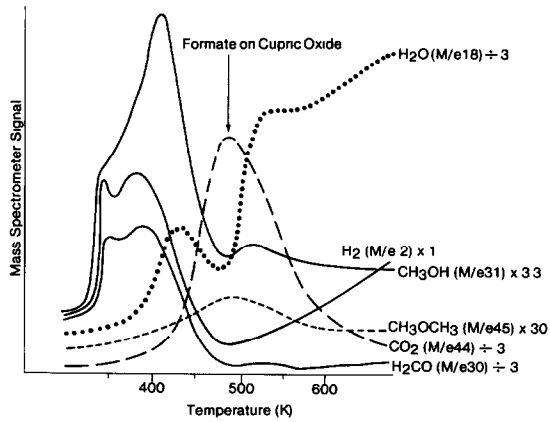
Figure 14
Time Dependent Infrared Spectra obtained by Co-dosing CO_2 and H_2 at 295K and Raising the Temperature to 390K ((a) initial spectrum - (f) final spectrum)



3.6. HCHO/Cu Adsorption and Reaction

The adsorption of formaldehyde on to partially oxidised polycrystalline copper gives rise to a number of adsorbed states. Formaldehyde is adsorbed molecularly. In addition to this, the molecularly held formaldehyde reacts with the surface oxygen to produce methoxy and formate species. These are evidenced on temperature programming by the coincident desorption of H_2, CH_3OH and HCHO at 340K (the methoxy species) and by the coincident desorption of CO_2 and H_2 at 440K (the formate species) (Figure 15) (28). This is the same formate species produced by CO_2 and H_2 co-adsorption described in Section 3.5. It can also be seen in Figure 15 that, when the formate species begins to decompose, methanol is formed. Therefore, as with zinc oxide (Section 2.6), the rate determining step in methanol synthesis on partially oxidised copper is the hydrogenation (or hydrogenolysis) of the adsorbed formate species. In the case of copper the activation energy of this rate determining step calculated from the peak maximum temperature is ~28 kcal mol^{-1} while for zinc oxide it is ~38 kcal mol^{-1}. In a copper/zinc oxide/alumina catalyst, therefore, if methanol were to be formed by parallel routes on both the zinc oxide and the copper, the copper route would dominate since it is the lower energy pathway.

Figure 15
Formaldehyde Adsorption on Cupric Oxide



3.7. ^{14}C Radiolabelling Studies

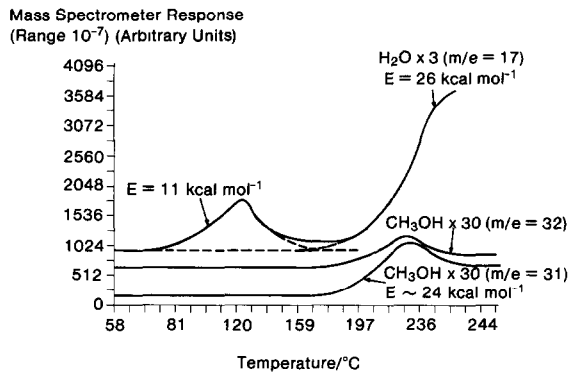
The prediction of these results is that on a $Cu/ZnO/Al_2O_3$ catalyst when methanol is being synthesised from a $CO/CO_2/H_2$ mixture it is the CO_2 component of the feed which forms the methanol. Radiolabelling experiments in which the CO_2 component of the feed was labelled with ^{14}C confirmed this prediction (32). (Earlier radiolabelling studies by Kagan and co-workers which came to the same conclusion went largely unheeded (10).)

3.8. $CO_2/H_2/Cu$ Reaction

The temperature programmed reaction spectrum obtained by passing a CO_2/H_2 mixture (8% CO_2, 1 bar) over polycrystalline copper while raising the temperature from ambient to 550K is shown in Figure 16 (20). Water evolution occurs in two distinct temperature regimes. The first, starting at about 70°C, is the reduction of surface oxygen resulting from the room temperature decomposition of the CO_2 on the copper (18). The second starting at ~170K°C is the reverse water gas shift reaction. Line shape analysis gives this reaction an activation energy of 26 kcal mol^{-1}.

Methanol also is formed, the temperature of the onset of which roughly coincides with the onset of the reverse shift reaction. Line shape analysis of the increase in methanol synthesis rate with temperature gave an activation energy of 24 kcal mol^{-1}. The maximum in the rate of methanol synthesis at ~500K is due to the reaction reaching equilibrium.

Figure 16
Temperature Programmed Reaction
Carbon Dioxide 8% and Hydrogen
(Jet Separator)



4. THE $Cu/ZnO/Al_2O_3$ CATALYST

4.1. CO/H_2 Co-adsorption on a Reduced $Cu/ZnO/Al_2O_3$ Catalyst

The adsorption isotherms produced by pulsing CO into a hydrogen stream over a reduced $Cu/ZnO/Al_2O_3$ catalyst in the temperature range 100-150°C are shown in Figure 17. The isosteric heats derived from these (Figure 18) lie in the range 11.5 to 12.3 kcal mol^{-1} which shows that, to an adsorbing CO molecule, the catalyst appears as low index face dominated polycrystalline copper.

Figure 17
CO Adsorption Isotherms on a Reduced
$Cu/ZnO/Al_2O_3$ Catalyst when Co-adsorbed
with H_2

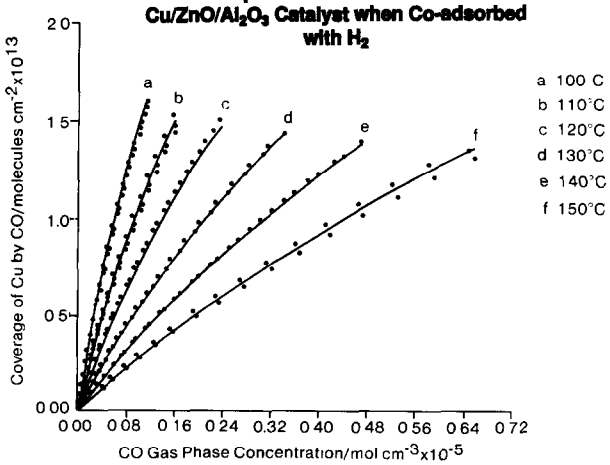
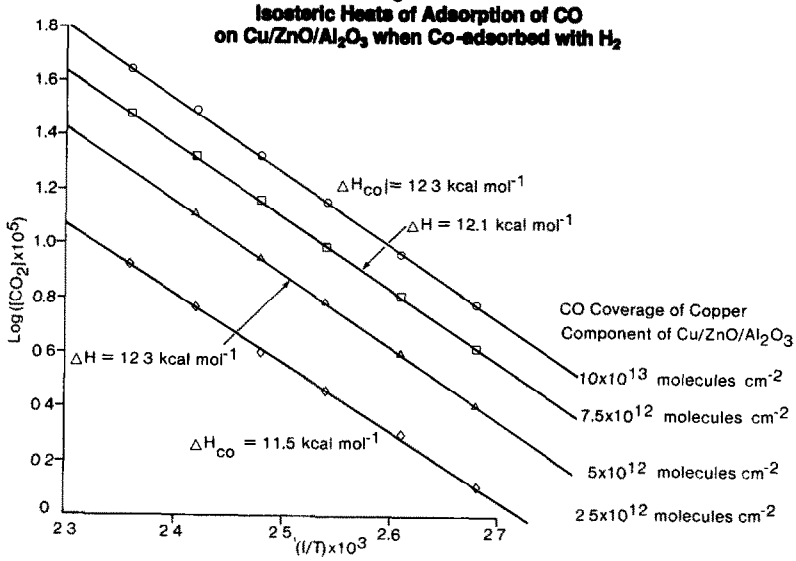


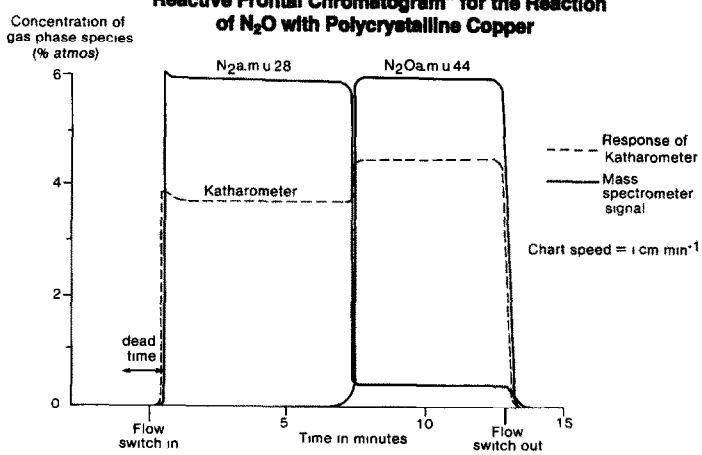
Figure 18
Isosteric Heats of Adsorption of CO on $Cu/ZnO/Al_2O_3$ when Co-adsorbed with H_2



4.2. Measurement of the Copper Metal Area by N_2O Decomposition

Because the catalyst appears to the adsorbing CO molecule as polycrystalline copper, it is apparent that the area of this copper could be an important catalytic parameter. The reaction of nitrous oxide with copper has been used to evaluate metal surface areas of pure copper and of supported copper catalysts. The method usually involved measuring the amount of nitrogen evolved in a static system by freezing out excess N_2O and determining the residual nitrogen pressure in a conventional volumetric apparatus (33, 34).

Figure 19
"Reactive Frontal Chromatogram" for the Reaction of N_2O with Polycrystalline Copper



We have developed a technique which we have termed, "reactive frontal chromatography" and have calibrated it against polycrystalline copper whose total area is measured in situ (35) by nitrogen adsorption. It involves passing a N_2O/He (6% N_2O) stream over the copper at 60°C monitoring the N_2 and N_2O continuously (Figure 19). The nitrogen evolution ceased when the oxygen coverage became ½ monolayer, in agreement with surface science studies which showed oxygen saturation by N_2O decomposition on the low index faces of copper (111, 110 and 100) to be ½ monolayer (36, 37, 38, 39).

4.3. $CH_3OH/Cu/ZnO/Al_2O_3$ Adsorption and Reaction

Figure 20
Methanol Adsorption on a $Cu/ZnO/Al_2O_3$ Catalyst

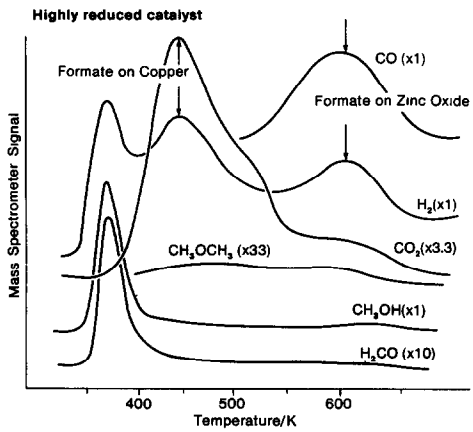
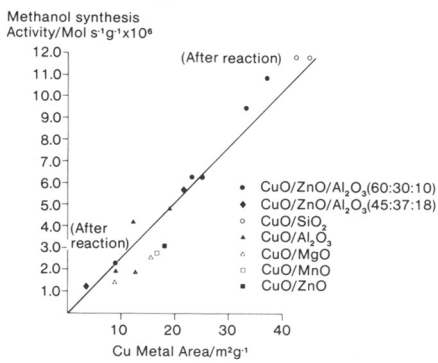


Figure 20 is the temperature programmed reaction spectrum obtained after the adsorption at room temperature, of methanol on a partially oxidised $Cu/ZnO/Al_2O_3$ catalyst. The most important features of this spectrum are:- (i) the coincident desorption of CO_2 and H_2 at 440K (the formate species on the copper component), (ii) the coincident desorption of CO, (CO_2 small) and H_2 at 580K (the formate species on ZnO) and (iii) the coincident desorption of H_2, HCHO and CH_3OH at 380K (the methoxy species on ZnO). The significance of this result is that the stability of the formate species on the copper and zinc oxide components of the catalyst is unaffected by these components being intimately mixed. Since the hydrogenation of the formate on each of these components separately is the rate determining step in methanol synthesis, it follows that no synergy accrues to the intimate mixture of copper and zinc oxide in terms of a lowering of the energy barrier to methanol synthesis on either of them. The catalyst appears to act rather prosaically as the sum of its parts, suggesting that parallel routes to methanol synthesis might be possible on each of the copper and zinc oxide components. (This, however, is found not to be the case (see Section 4.5)).

4.4. Methanol Synthesis Activity on a Series of Oxide Supported Copper Catalysts from $CO/CO_2/H_2$ Feeds at 50 bar

The rate of methanol synthesis produced from $CO/CO_2/H_2$ mixtures (generally 10:10:80) over a series of oxide supported copper catalysts which include SiO_2, MgO, Al_2O_3, ZnO and MnO together with ZnO/Al_2O_3 was measured at 240°C and at 50 bar. The copper metal area of each of these catalysts was determined by the technique of N_2O reactive frontal chromatography, described in Section 4.2. A plot of the methanol synthesis activity of each of these catalysts against their copper metal area is shown in Figure 21. This shows a significant correlation between methanol synthesis activity and copper area, the turnover member, i.e. the rate per copper site, being essentially identical for all the catalysts (1.6×10^{-2} molecules $CH_3OH\ s^{-1}$ site^{-1}). (The deviation of some of the points, notably the ones for the Cu/MgO, Cu/ZnO and Cu/MnO catalysts, from the straight line is an honest reminder of imperfect data. In mitigation however, it should be stated that the data for these points was taken in a different laboratory from the others, in equipment which did not have the capability of measuring the copper metal area in situ, it being noted from Figure 21 that a fraction of the initial copper area of many of catalysts was lost during reaction. Had the copper area of these catalysts been measured, in situ, after the catalyst had been producing methanol for the same time (5h say) it is probable that the activity area relationship would have been closer to the line.)

Figure 21
Methanol Synthesis Activity as a Function of Copper Metal Area



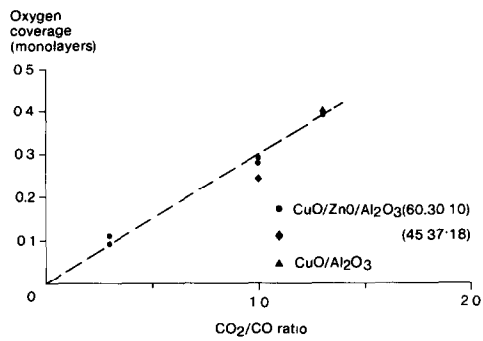
The conclusions are therefore:- (i) all of the copper is active and (ii) no unique synergy attaches to the copper/zinc oxide combination since copper supported on oxides as diverse as SiO_2 or MgO are equally active (40).

These findings were reproduced exactly by Griffin and co-workers (41). At 50 bar and 523K using a $CO/CO_2/H_2$ feed, they obtained an identical turnover number per copper site to the one quoted above. Furthermore they obtained a linear relationship for methanol synthesis activity with respect to copper metal area and also found that the activity per copper site for a silica supported copper catalyst was if anything slightly greater than that of the copper/zinc oxide catalyst leading them to conclude, "that ZnO does not play any exceptional role in determining the specific activity of the impregnated Cu catalysts".

4.5. The State of the Catalyst Surface during Methanol Synthesis

The oxygen coverage of the copper during methanol synthesis from $CO/CO_2/H_2$ mixtures (50 bar, 240°C) can be measured by two means. The first involves measuring the area after reduction but before reaction by N_2O decomposition. Re-measuring the area by the same technique after reaction, having cooled the catalyst to 60°C in helium so as to desorb the formate species and hydrogen, will determine the free copper area, the difference between the two being the oxygen coverage.

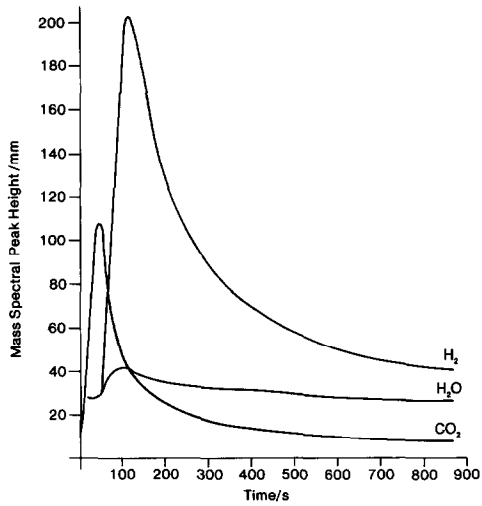
Figure 22
Steady State Oxygen Coverage of the Copper Surface under Methanol Synthesis Conditions as a Function of the CO_2/CO ratio



The oxygen coverage of the copper in monolayers determined by this method is shown in Figure 22 as a function of the CO_2/CO ratio. This shows that the coverage is a linear function of the CO_2/CO ratio, with the oxygen coverage approaching the saturation value (½ monolayer) for a CO_2/CO ratio of ~1.6. From this, the role of the CO can be seen to be to be that of a reductant keeping the copper in a more highly reduced (more active) state than can be produced by hydrogen reduction alone.

A second means of determining the oxygen coverage of the copper is simply by reduction with CO at 200°C having lowered the temperature from 250°C to that value under helium, allowing sufficient time (30 mins) for the desorption of formate and hydrogen. (In this instance the methanol was made from a CO_2/H_2/He (10:80:10) mixture (1 bar) at a rate of 1.9×10^{-9} mol s^{-1} g^{-1} or a turnover number of 3.0×10^{-6} molecule CH_3OH (Cu site)$^{-1}s^{-1}$.)

Figure 23
Reaction of a CO/He (10% CO) Stream at 200°C with 51-2 Catalyst producing CH_3OH from a CO_2/H_2/He Feed (10:80:10)

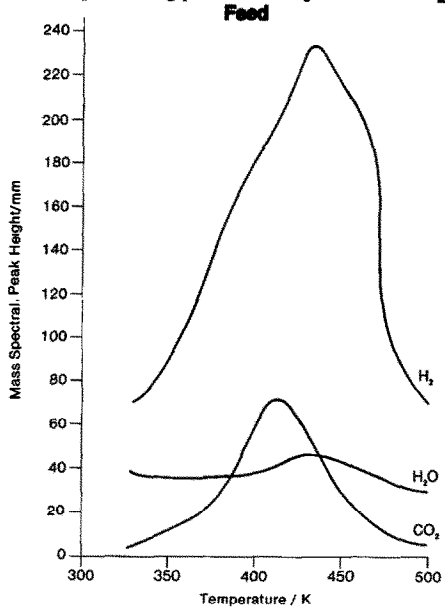


The result of such an experiment is shown in Figure 23. The total amount of CO_2 produced (oxygen atom coverage) is 2.9 x 10^{20} molecules, corresponding to an oxygen atom coverage 3.2 x 10^{14} atom cm^{-2}. If the oxygen from the small amount of water observed is added to this, the total oxygen atom coverage is 3.9 x 10^{14} atoms cm^{-2} or 78% of saturation.

The surprising feature of Figure 23 is the evolution of hydrogen. This occurs when roughly 40% of the oxygen is removed from the surface and in total amount corresponds to one hydrogen atom per surface copper atom. The rationale for its appearance is that the hydrogen is in fact sub surface (26), having been trapped in position by the restructured copper surface brought about by the oxygen overlayer (28). Lifting the reconstruction by removing the oxygen allows the hydrogen to evolve. Recent studies using a NMR technique (outlined in reference 42) have confirmed the existence of this subsurface hydrogen in the copper, being observed only where the copper is covered with an overlayer of oxygen (43).

Another means of probing the state of the catalyst surface during methanol synthesis is by temperature programmed desorption after the reaction, the temperature being lowered to ambient under the reaction mixture (CO_2/H_2/He 10:80:10, methanol synthesis rate 1.9 x10^{-9} mol s^{-1} g^{-1}) before temperature programming in a helium stream. The result of such an experiment is shown in Figure 24.

Figure 24
Temperature Programmed Desorption Spectrum from 51-2 Catalyst having produced CH_3OH from a $CO_2/H_2/He$ Feed

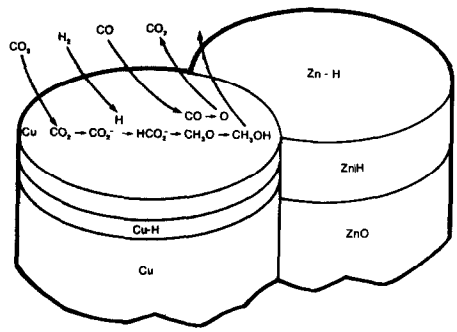


Carbon dioxide and hydrogen (shoulder) evolve coincidently at 440K (formate on copper). The coverage of the copper by the formate was 2.6 x 10^{14} ions cm^{-2} (26% of a monolayer). (This is probably greater than the formate population during methanol synthesis from the carbon dioxide/hydrogen/helium stream at 230°C since this temperature is well above the decomposition peak maximum.)

The hydrogen desorbing at temperatures above 440K can only derive from the zinc oxide component of the catalyst occurring as it does in too high a temperature regime to come from the copper. The total amount of hydrogen evolved was 1.2 x 10^{21} molecules or a coverage of the zinc oxide of 10 monolayers of hydrogen atoms (for an assumed zinc oxide area of 33 $m^2 g^{-1}$). Surprisingly, then, in the competitive adsorption of hydrogen and carbon dioxide (8:1, H_2:CO_2, 1 bar, 500K) on the zinc oxide component of the catalyst, the hydrogen wins and zinc oxide is hydrided or contains interstitial hydrogen atoms to a value equivalent to ten monolayers depth. This surface is thereby rendered inactive for formate formation and therefore for methanol synthesis on the zinc oxide (28).

Having removed the formate from the copper and the hydrogen from the zinc oxide by temperature programming, the oxygen coverage of the copper was again determined by CO reduction at 200°C. A time dependent evolution of CO_2 and hydrogen identical to that shown in Figure 23 was obtained, re-affirming the conclusion that the monolayer of hydrogen is under the surface of the copper. This is not desorbed by temperature programming and is only released having removed the oxygen from the surface of the copper, thus lifting the reconstruction (28).

Figure 25
Schematic Representation of the Mechanism of Methanol Synthesis over a Copper/Zinc Oxide/ Alumina Catalyst under Reaction Conditions



The standing composition of the operating catalyst is shown diagramatically in Figure 25. The copper is covered up to ~40% of a monolayer with oxygen atoms on top of which exists ~25% of a monolayer of formate species with a monolayer of hydrogen atoms under the surface of the copper. The zinc oxide surface is hydrided or contains interstitial hydrogen atoms to a depth of about ten monolayers.

5. ALTERNATIVE MODELS

5.1. The Junction Effect Theory

The view has been promulgated that, for oxide supported metal catalysts in general, and for zinc oxide supported copper in particular, the activity of these catalysts in methanol synthesis derives from the increase in the number of defects (anion vacancies) in the oxide, brought about by the stabilisation of these defects by the vicinal metal - the junction effect (44). Indeed, it has been proposed that the metal/oxide junction effect can produce a one thousand fold increase in the number of oxide defects. The exact role of these anion vacancies in the synthesis of methanol has not been completely specified in the junction effect theory other than as a site for hydrogen dissociation, which thereafter hydrogenate, somehow, carbon monoxide or carbon dioxide.

We are in complete agreement with Frost that the anion vacancies are the sites for methanol synthesis on zinc oxide (11). As outlined in section 2.8, we have shown, the mechanism of methanol synthesis on zinc oxide from $CO/CO_2/H_2$ mixtures to be by adsorption of CO_2 at the defect where it becomes CO_2^-. Hydrogenation thereafter is facile, first to formate, the longest lived intermediate, and then

to methoxy and methanol. The role of the carbon monoxide component is to remove the oxygen anion from the lattice, thus creating the defect.

However when the adsorbate coverage of a copper/zinc oxide/alumina catalyst which had been producing methanol was interrogated by temperature programmed desorption, the only intermediate observed was that of the formate adsorbed on copper (28), consistent with our finding of a linear relationship between copper metal area and methanol synthesis activity for a range of oxide supported copper catalysts (40). No formate was adsorbed on the zinc oxide component of the catalyst and so in the case of the copper/zinc oxide/alumina system, the junction effect theory does not apply.

5.2. Models Involving the Concept of Synergy

Synergy is a beguiling concept in catalysis. It contains within it elements of the philosopher's stone. Two materials which of themselves are inactive, in combination, produce a highly active catalyst. Copper and zinc oxide were, and in some instances still are, thought to be such a synergistic combination in respect of methanol synthesis.

5.2.1. Substitution of Cu^{+} for Zn^{2+} in the Zinc Oxide Lattice

Klier sought to explain his observation of the activity of the copper/zinc oxide combination relative to his observation of the total inactivity of copper and the low activity of zinc oxide in the thesis that the active centre in the copper/zinc oxide combination was the Cu^{+} species in the zinc oxide lattice (5-9) (see introduction). This unique species was considered to bond the carbon monoxide more strongly than the Zn^{2+} or the Cu^{2+} due to its greater ability to back donate to the carbon monoxide from the d-orbitals, the carbon monoxide being considered to be the precursor to methanol. The observation that it was the carbon dioxide molecule in the $CO/CO_2/H_2$ feed which was the direct precursor to methanol (10, 32), and of the linear relationship between methanol synthesis activity and copper metal area (40) largely discredited this view. (The ability to measure the metal area of supported metal catalysts in situ can be seen by this example to be of comparable importance as that of the total area of the catalyst.)

5.2.2. Synergy at a Distance

Burch and co-workers in a series of papers (45-50) have sought to construct an explanation of their observation of an increase in the rate of methanol synthesis from a $CO/CO_2/H_2$ feed over a physical mixture of silica supported copper and silica supported zinc oxide relative to the rate obtained on Cu/SiO_2 alone (45). This increase in rate was observed only when CO_2 was included in the feed and was not observed with a CO/H_2 feed (45).

Several theses were suggested; all involved the transport of one adsorbed specie from the copper to the zinc oxide and back again. The species considered were hydrogen atoms either through the gas phase or by spillover. The transport of hydrogen atoms from the copper to the zinc oxide by spillover and transport back as a hydroxyl specie was also considered (47). The view ultimately decided upon was that it was hydrogen atoms which migrated from the copper to the zinc oxide, the latter acting as a sink for the hydrogen atoms for their ready transference back to the copper to hydrogenate the formate species to methanol.

Recently, their inability to observe a formate by Fourier transform infrared spectroscopy after dosing a $CO/CO_2/H_2$ mixture on to the Cu/SiO_2 catalyst at 325K and 14 bar has caused them to question its involvement in the methanol synthesis

reaction (51). (This last result flies in the face of a vast body of evidence (28, 30, 52-54) that the formate on copper is crucially involved in the reaction and must be regarded as an artefact.)

The difficulties with the concept of hydrogen spillover from the silica supported copper to the zinc oxide supported on a separate silica particle are twofold. Firstly, it is hard to see that there would be sufficient points of contact in the physical mixture to provide an adequate pathway for the migration. Secondly, the necessity of requiring the zinc oxide to act as a source of hydrogen to the copper is doubtful, bearing in mind that the hydrogen must first adsorb on the copper before migrating to the zinc oxide. Indeed, were it to happen, it could easily be envisaged that it would induce an oscillatory reaction - a feature that has never been observed. The dissociative sticking probability of hydrogen on copper at 500K is $6x10^{-3}$ (this sticking probability of $6x10^{-3}$ at 500K is calculated on the basis of a 5 kcal mol^{-1} activation energy to hydrogen adsorption (22)) which at 50 bar in 80% hydrogen, results in the adsorption rate of $2x10^{8}$ monolayer s^{-1}. On that basis there is surely no need for the zinc oxide to act as a source of hydrogen to the copper. Indeed the equilibrium coverage of the hydrogen on the copper in 40 bar hydrogen at 500K is unity. (This latter calculation is made on the basis of a 5kcal mol^{-1} activation energy to adsorption (22) and a 15 kcal mol^{-1} desorption activation energy, Tm ~ 300K - Figure 10).

The problem of explaining the increased rate of methanol synthesis of physical mixtures of silica supported copper and zinc oxide remains. On the basis that the activity of copper based catalysts is a linear function of the copper area, the suggestion was made that some re-distribution of the copper must be occurring leading to an increase of the copper area (55). Burch and co-workers (45, 56), however, claimed to have examined the ZnO/SiO_2 particles after reaction and to have found no copper. Recently, though, Frost (57) repeated Burch's experiment and found evidence for the migration of the zinc oxide to the copper. This would be a high area ZnO which could stabilise a higher area of copper by migration of the copper over the zinc oxide.

6. CONCLUSIONS

Methanol has been shown to be formed from the carbon dioxide molecule of a $CO_2/CO/H_2$ feed. The active constituent of the $Cu/ZnO/Al_2O_3$ catalyst is the copper component, a linear relationship having been established between methanol synthesis activity and the copper metal area of a series of oxide supported copper catalysts.

The carbon dioxide molecule adsorbs, dissociatively, on the copper component of these catalysts to form a symmetric carbonate species which is hydrogenated to a bidentate formate - the longest lived intermediate in methanol synthesis. The rate determining step in methanol synthesis is the hydrogenation of the bidentate formate species. The role of the carbon monoxide molecule of the $CO/CO_2/H_2$ feed is to keep the copper in a more highly reduced (more active) state than could be produced by reduction with hydrogen alone. Indeed the oxygen coverage of the copper is a function of the CO/CO_2 ratio.

Methanol can be synthesised from CO/H_2 feeds on $Cu/ZnO/Al_2O_3$ catalysts but by a factor of $\sim 10^2$ slower in rate than can be achieve using CO_2/H_2 feeds. No intermediate has ever been identified by temperature programmed desorption for the CO/H_2 interaction to form methanol. This implies that the intermediate (probably a formyl species) is weakly held to the surface so that its standing concentration at reaction temperatures is considerably lower than that of the formate species.

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